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(54) Title: FIBER GLASS COMPOSITION HAVING LOW IRON OXIDE CONTENT

(57) Abstract

Calcia-alumonosilicate glass and fiber glass compositions formed by adding at least one alkaline earth metal component to naturally occurring zeolite. The alkaline-resistant fiber glasses formed from such a batch have a low iron oxide content and may be added to cementitious bodies for reinforcement.

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FIBER GLASS COMPOSITION HAVING LOW IRON OXIDE CONTENT

Technical Field

The invention herein relates to alkaline-resistant glasses. While it pertains to glass bodies generally, it has particular pertinence to glasses which are fiberizable.

Background Art

The natural mineral zeolites are a group of hydrous alkali and/or alkaline earth aluminosilicates which have an open three-dimensional crystalline framework. While a large number of individual mineral zeolites are known and have been described in the literature, eleven (11) minerals make up the major group of mineral zeolites: analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, natrolite, phillipsite and wairakite. The chemical and physical properties of these major mineral zeolites, as well as the properties of many of the minor mineral zeolites, are described extensively in Lefond (ed.), Industrial Minerals and Rocks (4th Ed., 1975), pp. 1235-1274; Breck, Zeolite Molecular Sieves (1974), especially Chapter 3; and Mumpton (ed.), Mineralogy and Geology of Natural Zeolites, Vol. 4 (Mineralogical Society of America: November, 1977). These publications also describe the geologic occurrence of the natural mineral zeolites and some industrial and agricultural uses which have been proposed or in which the natural mineral zeolites are now being used commercially.

It is important to note that the natural mineral zeolites are an entirely different class of materials from the "synthetic zeolites" which have been widely described in many recent articles and patents. Because there is no universally recognized system for

naming the synthetic zeolites, and because some of the synthetic materials exhibit x-ray diffraction patterns which suggest possible similarities in structure with the natural mineral zeolites, some reports in the literature and patents have described certain synthetic zeolites as "synthetic" versions of the natural mineral zeolites. Thus, for instance, certain synthetic zeolites have been described as "synthetic analcime" or "synthetic mordenite" and so forth. As noted in the aforementioned Breck reference, however, this approach is technically unsound and has merely led to confusion between the two (2) otherwise distinct classes of materials: the natural mineral zeolites and synthetic zeolites. While it has been recognized that there are structural similarities between the two groups, it is clear that the natural mineral zeolites constitute a class of materials significantly separate and distinct in structure and properties from the synthetic zeolites.

Glasses are vitreous materials composed largely of silica. Because silica is a highly refractory material, however, substantial quantities of soda ash, lime or other fluxing materials are added to the silica to permit the glass-forming composition to be melted at reasonable temperatures. Small quantities of other materials, usually elemental materials or oxides, are commonly added to glass melts to provide particular properties such as color or chemical resistance to the finished glass. Heretofore, however, there has not been any report of significant usage of zeolites in glass matricies and particularly as the principal component of a glass matrix. One experiment has been reported in which a clinoptilolite and glass mixture was fired at 800°C (well below the melting point of either) to produce what was described as a porous low density glass composition; see Mumpton, supra, p. 197, referring to Tamura Japanese published application 74/098,817 (1974).

Alkaline resistance is provided in some glasses by the inclusion of zirconia and/or titania, such as in AR glasses of Pilkington. Although these materials enhance the alkaline resistance of glass bodies, these are refractory materials which increase the melting point of such glasses. Also, zirconia and titania tend to add cost to the glass inasmuch as these are much more expensive materials than silica, soda, calcia and the usual components of soda lime silica glasses.

Although calcia tends to lower the melting point of the glass composition, a general admonition exists in the glass technology against using calcium oxide in soda lime silica glasses in quantities greater than about fifteen percent (15%) by weight of the glass body.

Disclosure of the Invention

Objects of the Invention: It is an object of the invention to produce low iron oxide, alkaline-resistant glasses from modified, naturally occurring zeolite materials.

Another object of the invention is to modify naturally occurring zeolite materials with readily available alkaline earth compounds.

A further object of the invention is to form glass bodies from modified naturally occurring zeolites at relatively low temperatures.

A still further object of the invention is to form compositions having improved properties, in particular, fiberizability and/or alkaline resistance.

Summary of the Invention: The invention herein comprises glass compositions which have outstanding resistance to alkaline environments. Such glass compositions are characterized by a relatively high calcia

content and a relatively low silica content and a very low iron oxide content. In particular, these glass compositions are derived from selected or treated naturally occurring zeolites to which alkaline earth compounds, especially calcium compounds or calcium and magnesium compounds are added to yield a low-silica, high-alkaline earth oxide, especially calcia, glass composition. Also included within the scope of the present invention are glass bodies, particularly fibers, formed from the aforesaid glass composition.

Detailed Description and Best Modes for Carrying Out Invention

The present invention relates to low iron oxide, alkaline-resistant fiber glasses containing relatively high quantities of one or more alkaline earth oxides and particularly to glasses comprising silica, alumina, calcia and combinations of calcia and magnesia. A particularly useful alkaline-resistant glass has the following composition:

Silica - about 30% to about 60% by weight, alumina - about 2% to about 10% by weight, calcia - about 18% to about 60% by weight, magnesia - about 0% to about 30% by weight wherein the calcia plus magnesia content is from about 20% to about 60% by weight, and the iron oxide content is less than about 0.5% by weight.

It is significant, as described hereinafter, that such glasses may be easily and inexpensively formed by melting a calcium compound, in the form of limestone, for example, or a calcium compound and a magnesium compound, such as found in dolomite, with a selected or treated naturally occurring zeolite. However, glasses of excellent resistance to alkaline attack may be formed by starting with conventional materials such as silica, soda ash, an aluminate, limestone and/or dolomite. Such glasses may be described as low-alumina, calcium silicate

glasses inasmuch as the calcium, in many instances, is present in about the same quantity, on a weight basis, as is the silica.

The alkaline-resistant glass composition may be readily formed by mixing calcium carbonate with a naturally occurring zeolite material. Many naturally occurring zeolite materials may be formed into glasses under appropriate conditions. The zeolites, as a glass-forming material, have many advantages. Naturally occurring zeolites have already undergone reaction and the various elements are intimately mixed and reacted with one another. Also, the zeolite materials are particularly useful inasmuch as they have a very low sulphur content. In particular, very useful glass bodies may be formed by combining various quantities of calcia or calcia and magnesia combinations with a zeolite of the following compositional range:

Silica - about 60% to about 85%, alumina - about 6% to about 10%, Fe_2O_3 - about 1% to about 3%, calcia - about 0% to about 15%, magnesia - about 0% to about 5%, potassia - about 1% to about 5%, soda - 1% to 5%, with the percentage expressed being in weight per cent.

Naturally occurring, pre-reacted zeolites useful in the instant invention are those specially selected or treated to have a low iron oxide (FeO + Fe_2O_3 + Fe_3O_4) content. Preferred naturally occurring zeolites are those having an iron oxide content no greater than about 1.5% by weight and especially those with an iron oxide content less than about 1% by weight. Some deposits of naturally occurring zeolites contain less iron oxide than other deposits. For the purposes of this invention, zeolites with a low iron oxide content are preferred.

The iron oxide content of naturally occurring zeolites may be lowered by chemical and/or mechanical treatment. Often iron oxide is present in deposits as magnetite, which may be separated by magnetic means. Naturally occurring zeolite materials are finely ground and conveyed over a magnetic separator to reduce the iron oxide content to a value less than about 1.5% by weight and preferrably below 1% by weight.

A further means of treating the zeolite material involves dilution with very pure silica, alumina, and the like. For example, while glasses of various types may be formed from zeolite materials without addition of any other materials or by minor additions of selected materials to achieve certain properties in the resulting glass body. For purposes of the instant invention it is preferred that the zeolite material comprise less than about 50% of the batch materials. In the event that the zeolite materials are the only iron oxide containing materials in the batch, then the zeolite proportion with respect to other materials present should be selected to be such that the iron oxide content of the resulting glass is about 0.5% by weight or less, and particularly preferably less than about 0.4% by weight.

In particular, it has been found that additions of from 30% to about 70% by weight, and in particular from about 30% to about 60% by weight calcium carbonate mixed with a selected or treated zeolite results, after melting of the finely ground material, in a glass having excellent resistance to an alkaline environment. Furthermore, these glasses advantageously melt at temperatures from about 1250°C to about 1500°C. Also, glasses formed by mixing a selected or treated zeolite with similar weight percentages of dolomite, i.e. about 30% to 70% by weight of dolomite, result in glasses having comparable

properties to those formed by addition of calcium carbonate. Although carbonates are preferred reactants, other salts or compounds of alkaline earth metals, especially calcium and magnesium, could be utilized.

A glass-forming composition may be readily formed by mixing finely ground limestone with a finely ground zeolite material, such as the composition identified above. The zeolite material, inasmuch as it is a pre-reacted crystalline material, largely calcium aluminum silicates, reacts readily and efficiently with the calcium carbonate of the limestone to form a glass composition having a high calcia loading. Calcia loadings of about 30% to 50% calcium carbonate tend to provide slightly lower melting points than loadings involving 60% to 70% by weight calcium carbonate, based upon a weight of 100% equalling the total weight of the zeolite and calcium carbonate in the glass batch materials.

The glass material, upon cooling, exhibits good physical properties, having strengths and other qualities substantiallyequivalent to a typical soda-lime silicate glass and having resistance to alkaline solutions from about ten-fold to twenty-fold better than a typical soda-lime silicate window glass. Also, the resistance to alkaline materials tends to increase as the calcia content increases from about 30% to about 50% by weight of calcium carbonate in the mix and then tends to decrease slightly with loadings of 70% calcium carbonate contributing less resistance to dilute caustic soda than a glass with 30% loading.

Besides increasing the durability of the glass in alkaline environments, glasses having a relatively high calcia content have other advantages as well. The calcia addition tends to even out variances in the zeolite composition. Zeolites are naturally occurring

materials and are not homogenous nor uniform in their composition. Also, the zeolites contain iron which tends to contribute a brown color to the glass. Calcia, on the other hand, tends to contribute a light green color, which for many purposes is preferable to brown colored glass.

The zeolites contain relatively substantial quantities of water, that is, hydrated materials. Hydrated crystalline materials generally tend to melt at a lower temperature. Thus, there are further advantages to beginning the glass-forming operation with a pre-reacted zeolite, rather than initiating it with silica.

The melting ranges of the calcia-modified aluminum silicate glasses of this invention come within a range, i.e. about 1250°C to about 1500°C, which permits the drawing of glass fibers through platinum dies. The glass fibers could also be formed by spinning or other techniques. However, formation of continuous strands is best accomplished by drawing through an orifice in a platinum or platinum-rhodium body.

Fibers of the glass compositions of this invention are particularly useful inasmuch as they may be used to strengthen bodies which are highly alkaline in nature, for example, cement and plaster. Such fibers may also be used to strengthen organic matrices of various types. Reinforcement of cement with such fibers, however, provides a particularly advantageous use inasmuch as asbestos has been frequently used heretofore for that purpose. Because of various health and/or environmental concerns, the use of asbestos is being discontinued. Continuous strands or mats of glass fibers having the glass compositions described herein effectively reinforce cementatious, e.g. cement and concrete, bodies.

EXAMPLE I

A glass composition was prepared utilizng silica, alumina, calcium carbonate, magnesium carbonate, soda, and potassia. Various amounts of iron oxide were added to this glass composition as indicated in Table I.

TABLE I

The Crystallization Tendency of AR-Glasses

	Type Ia	Type Ib	Type Ic	Type Id	Type Ie	Type If
Fe_2O_3 addition	0.0%	0.1%	0.25%	0.5%	1.0%	1.5%
SiO_2	47.5	47.5	47.4	47.3	47.1	46.8
Al_2O_3	7.6	7.6	7.6	7.6	7.5	7.5
Fe_2O_3	0.0	0.1	0.25	0.5	1.0	1.5
CaO	34.6	34.6	34.5	34.4	34.3	34.1
MgO	7.7	7.7	7.7	7.7	7.6	7.6
K_2O	1.3	1.3	1.3	1.3	1.3	1.3
Na_2O	1.2	1.2	1.2	1.2	1.2	1.2
Melting Temp. (°C)	1400	1400	1400	1400	1400	1400
Melt Stability	excel.	excel.	good	good	fair	fair

The melting temperature for each glass composition was about 1400° C regardless of the minor quantities of iron oxide included in the batch.

The melt stability of the glasses was generally acceptable so long as less than about 0.5% by weight iron oxide was present.

The glass composition set forth in Table I is very similar to the composition obtained from a naturally occurring zeolite to which a substantial quantity of calcium carbonate and a small amount of magnesium carbonate have been added.

Similar results can be achieved from similar glass compositions prepared from a naturally occurring

zeolite which has been treated mechanically or chemically to have a low iron content or diluted with other ingredients having substantially no iron oxide content.

EXAMPLE II

Various glass compositions were prepared from substantially uncontaminated ingredients having essentially zero iron oxide content. The compositions and properties of such glass are set forth in Table II.

TABLE II

	Type A	Type B	Type C
SiO_2	48	50	50
Al_2O_3	8	10	15
CaO	35	35	30
MgO	8	5	5
Fe_2O_3	--	--	--
Melting Temp. °C	1450	1450	1500
Alkali resistance (5% NaOH, wt loss %)	0.7	0.9	
Fiberizability	fair	good	good
Working range	30	50	80

The glasses set forth in Table II are somewhat more refractory than the glass composition of Example I. Alkaline resistance of these glasses diminished with increasing silica + alumina content and/or lower CaO plus MgO content. The alkali resistance of Glasses IIA and IIB was outstanding.

Other adjustments in the proportions of oxides present in the resulting glass material may be made by utilizing different starting materials or by varying the proportions of ingredients in the glass-forming batch. Also, other ingredients may be added to alter the composition to be less refractory without adversely affecting fiberizability and stability of the glass melt. Such ingredients include fluxes such as soda, potassia and the like and boria.

The presence of substantial quantities of iron oxide may be tolerated in glasses formed into beverage containers and various other non-optical grade, non-fibrous uses. However, the presence of iron oxide as 0.5% by weight, and especially about 1.0% by weight, of a glass melt renders the melt relatively unstable and subject to spontaneous and rapid crystallization over a wide range of temperatures. Glasses of this invention, however, containing less than about 0.5% by weight, particularly less than about 0.4%, and especially less than about 0.25% by weight, are sufficiently stable that such molten glasses may be readily formed into continuous vitreous fibers.

Preferred glass compositions for the purpose of the invention have a silica content of about 45% to about 60% by weight, and especially about 45% to about 55% by weight; an alumina content of about 10% to about 20% by weight, and especially about 12% to about 18% by weight; a calcia content of about 20% to about 35% by weight, and especially about 22% to about 35% by weight; a magnesia content of about 0% to about 10% by weight, and especially about 0% to about 5% by weight; wherein the CaO+MgO content is about 22% to about 35% by weight, and especially about 25% to about 30% by weight.

Some glass compositions may be less affected by the presence of iron oxide than the glasses of the inven-

tion, which are characterized by a relatively high alkaline earth metal oxide content, especially a high calcia content. These glasses have excellent alkaline resistance and may be readily formed from naturally occurring, pre-reacted zeolites modified with readily available materials such as limestone and dolomite.

Industrial Applicability

The outstanding tolerance to alkaline environments render these glasses, especially in fiber or flake form, as excellent reinforcement materials for concerete, plaster and other inorganic matrices of an alkaline nature. This is especially significant inasmuch as asbestos, which has been a standard extender as reinforcement material in cement and concrete bodies, is considered undesirable because of the health hazard it may present.

Glass fibers formed from glasses of this invention have particular utility as a reinforcement material for cementatious bodies, e.g. cement and concrete. Cementatious bodies exhibit enhanced strength when such bodies are reinforced with a minor amount of glass fiber, preferably from about 1% to about 10% by weight, and more preferably about 1.5% to about 7.5% by weight glass fibers of the type described herein. The fibers are included in cementatious bodies in sufficient amount to enhance the strength of such bodies.

The glasses of this invention have excellent resistance to moisture degradation and do not degrade or deteriorate during normal or extended storage periods.

The low sulfate content of naturally occurring zeolites is important in their utilization as ingredients in glass-forming processes. Sulfates tend to degrade during glass melting conditions, yielding sulfur dioxide and other objectionable sulfur compounds. Environmental

concerns militate against use in glass-making processes of any raw material containing sulfates, sulfites and other sulfur compounds.

Zeolite materials provide an excellent source of silica and minor quantities of alumina, calcia and the like. Very useful glasses may be formed from glass-forming batches having at least about 20% by weight of a zeolite material present. Frequently, 35% by weight up to about 70% by weight of a zeolite material may be advantageously included in a glass-forming batch.

Although the instant invention has been described as having relatively high loadings of calcia, it is to be recognized that at least minor substitutions of other alkaline earth metal oxides in lieu of calcia may be made. For example, magnesium compounds, particularly magnesium carbonate may be substituted for at least some of the calcium carbonate in preparing a batch for melting into an alkaline-resistant glass. Similarly, barium and strontium compounds may be substituted as well as beryllium compounds, many of which are naturally occurring materials found in the same geographic regions as zeolites.

The oxides of alkaline earth metal elements are not considered glass formers, which is a term applied to elements having a valence greater than three, e.g. silicon, boron, andphosphorous, which may form three-dimensional networks with their oxides, namely, silica, boric oxide, and various oxides of phosphorous. Alkaline earth metal elements, being divalent, are more tightly bound in a glass than are alkali metal elements.

Sources of alkaline earth metals to form oxides in the glasses of this invention are as follows:

Alkaline Earth Metal Compound	Source
Calcium Carbonate	Limestone Marble Chalk
Magnesium Carbonate	Dolomite
Magnesium Silicate	Serpentine
Barium Carbonate	Wetherite
Strontium Carbonate	Strontianite
Beryllium Aluminum Silicate	Beryl

Sources of calcium and magnesium carbonates are generally more plentiful and cheaper than sources of barium, strontium or beryllium compounds. Also, beryllium metal is considered toxic, although beryllium oxides bound within a glass body are not hazardous.

It is noteworthy that the zeolite-derived glasses of this invention have good working properties and strength in addition to outstanding alkaline resistance. These glasses may be used in any form, e.g. containers, sheets, and the like, and especially as fibers. These low iron oxide glasses may be used as flakes, bubbles (microspheres), fibers and the like to reinforce organic or inorganic matrices, especially cement, plaster and the like.

Aluminum may be included in the glass batch as alumina; aluminum silicates, e.g. from aluminosilicate glass cullet; or as naturally occurring materials such as kaolin, montmorillonite, and the like.

Zirconia may optionally be present in the fiber glass. Minor quantities of zirconia in the glass may result from melting the glass in zirconia containing crucibles or through the addition of a zirconium component such as zircon or a zirconium silicate or zirconia containing glass cullet.

Soda and potassia are often present in the glasses of the instant invention in amounts up to about 5% by weight of either, with amounts of about 1% to about 3% by weight of each being present and a combined amount of about 2% to about 5% by weight being usual. In instances that boria is present, the total soda, potassia, boria content is within the range of about 3% to about 10% by weight.

Claims

1. An alkaline-resistant glass comprising: silica - about 30% to about 60% by weight; alumina - about 2% to about 20% by weight; calcia - about 18% to about 60% by weight; magnesia - about 0% to about 30% by weight; and wherein calcia plus magnesia is about 20% to about 60% by weight, and the iron oxide content of said glass is less than about 0.5% by weight (calculated as FeO).

2. The glass of Claim 1 wherein the alumina content is in the range of about 10% to about 20%, and the Fe_2O_3 content is less than about 0.25% by weight.

3. The glass of Claim 1 wherein the calcia content is in the range of about 22% to about 60% by weight.

4. The alkaline-resistant glass composition of Claim 1 wherein the respective ingredients are present in the following amounts: silica - about 45% to about 60% by weight; alumina - about 12% to about 20% by weight; calcia - about 22% to about 30% by weight; magnesia - about 0% to about 10% by weight; and wherein calcia plus magnesia is about 22% to about 35% by weight.

5. A glass batch composition for forming the glass composition of Claim 1 which comprises at least about 20% by weight of said batch as at least one naturally occurring, prereacted zeolite.

6. The glass batch composition of Claim 5 wherein said glass batch composition includes at least one added alkaline earth metal component.

7. The glass batch composition of Claim 6 wherein said zeolite is present as about 20% to about 70% by weight and said glass composition includes at least one added aluminum component.

8. The glass batch composition of Claim 7 wherein said glass batch includes an added component of aluminum.

9. The glass batch composition of Claim 8 wherein said glass batch composition includes an added boron component.

10. An alkaline resistant fiber glass comprising:
SiO_2 - about 45% to about 55%;
Al_2O_3 - about 12% to about 18%;
CaO - about 22% to about 30%;
MgO - about 0% to about 10%;
wherein CaO + MgO is about 22% to about 35% and wherein said glass has an iron oxide content less than about 0.5% by weight.

11. The fiber glass of Claim 10 wherein the CaO + MgO content is about 25% to about 30%.

12. The fiber glass of Claim 10 wherein the iron oxide content is less than about 0.25%.

13. The fiber glass of Claim 11 wherein the glass consists essentially of silica, alumina, calcia,

and magnesia in the stated amounts and minor quantities of soda and/or potassia and boria.

14. In a calcia aluminosilicate fiber glass formed from glass batch materials containing substantial quantities of silicon, aluminum, and calcium components, the improvement comprising selecting components which have a sufficiently low iron content such that the resulting fiber glass has an iron oxide content of less than about 0.5% by weight.

15. The improvement of Claim 14 werein said iron oxide content is less than about 0.25% by weight.

16. The improvement of Claim 15 wherein said iron oxide content is less than about 0.1% by weight.

17. The improvement of Claim 14 wherein a substantial quantity of said silicon, aluminum and calcium component content is provided by a naturally occurring, pre-reacted zeolite.

18. The improvement of Claim 14 wherein said zeolite is present as at least about 20% by weight of said glass batch materials.

19. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 1.

20. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 2.

21. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 3.

22. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 4.

23. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 10.

24. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 12.

25. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 14.

26. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 15.

27. A cementatious body containing a minor amount of glass fibers containing the composition of Claim 16.

AMENDED CLAIMS
(received by the International Bureau on 28 March 1985 (28.03.85)

1. A composition useful for forming glass fibers having high alkaline resistance comprising:

a substantial quantity of naturally occurring pre-reacted zeolite, said zeolite comprising minor quantities of iron, sodium and potassium, and substantial quantities of silicon, aluminum, magnesium and calcium components capable of forming silica, alumina, magnesia and calcia under glass-forming conditions;

significant quantities of aluminum and calcium components capable of forming alumina and calcia under glass-forming conditions, said aluminum and calcium components being in addition to any such components present in said zeolite being essentially free of iron;

wherein the proportion of said additional aluminum and calcium components to said zeolite being such that said glass fibers comprise less than about 0.5% by weight iron oxide, calculated as FeO.

2. The composition of claim 1 wherein said zeolite comprises less than about 1.5% by weight iron oxide, said iron oxide comprising FeO, Fe_2O_3 and Fe_3O_4.

3. The composition of claim 2 wherein said zeolite comprises less than about 1% by weight iron oxide.

4. The composition of claim 1 wherein said composition comprises additionally a boron compound, which is essentially free of iron, in amounts such that said glass fibers comprise a soda, potassia and boria content of about 3% to about 10% by weight.

5. The composition of claim 1 wherein said zeolite and said additional aluminum and calcium components are present in proportions such that said glass fibers comprise about 30% to about 60% by weight silica, about 2% to about 20% by weight alumina, about 18% to about 60% by weight calcia, about 0% to about 30% by weight magnesia, and about 20% to about 60% by weight calcia plus magnesia.

6. The composition of claim 5 wherein said glass fibers comprise about 10% to about 20% by weight alumina and less than about 0.25% by weight Fe_2O_3.

7. The composition of claim 6 wherein said glass fibers comprise from about 20% to about 35% by weight calcia.

8. The composition of claim 7 wherein said glass fibers comprise about 45% to about 60% by weight silica, about 22% to about 35% by weight calcia, about 0% to about 10% by weight magnesia, and about 22% to about 35% by weight calcia plus magnesia.

9. The composition of claim 8 wherein said glass fibers comprise from about 45% to about 55% by weight silica, and about 12% to about 18% by weight alumina.

10. The composition of claim 9 wherein said composition comprises about 25% to about 30% calcia plus magnesia.

11. The composition of claim 9 wherein said composition comprises less than about 0.25% iron oxide.

12. The composition of claim 10 wherein said glass fibers consist essentially of silica, alumina, calcia,

magnesia, and minor quantities of soda and/or potassia and boria.

13. The composition of claim 1 wherein said composition comprises at least about 20% by weight said zeolite.

14. A cementatious body containing a minor amount of said glass fibers of claim 1.

15. The cementatious body of claim 14 wherein said zeolite and said additional aluminum and calcium components are present in proportions such that said glass fibers comprise about 30% to about 60% by weight silica, about 2% to about 20% by weight alumina, about 18% to about 60% by weight calcia, about 0% to about 30% by weight magnesia, and about 20% to about 60% by weight calcia plus magnesia.

16. The cementatious body of claim 15 wherein said glass fibers comprise about 10% to about 20% by weight alumina and less than about 0.25% by weight Fe_2O_3.

17. The cementatious body of claim 16 wherein said glass fibers comprise from about 20% to about 35% by weight calcia.

18. The cementatious body of claim 17 wherein said glass fibers comprise about 45% to about 60% by weight silica, about 22% to about 35% by weight calcia, about 0% to about 10% by weight magnesia, and about 22% to about 35% by weight calcia plus magnesia.

19. The cementatious body of claim 18 wherein said glass fibers comprise from about 45% to about 55% by weight silica and about 12% to 18% by weight alumina.

20. The cementatious body of claim 18 wherein said glass fibers comprises less than about 0.25% iron oxide.

21. In a calcia aluminosilicate fiber glass formed from a composition containing substantial quantities of a naturally occurring zeolite, and additional aluminum and calcium components, the improvement comprising:

selecting said components which have a sufficiently low iron content such that said fiber glass comprises less than about 0.5% by weight iron oxide.

22. The improvement of claim 21 wherein said fiber glass comprises less than about 0.25% by weight iron oxide.

23. The improvement of claim 22 wherein said glass fiber comprises less than about 0.1% by weight iron oxide.

24. The improvement of claim 21 wherein a substantial quantity of silicon, aluminum and calcium of said fiber glass is provided by said zeolite.

25. The improvement of claim 21 wherein said composition comprises at least about 20% by weight said zeolite.

26. A cementatious body containing a minor amount of glass fibers of said fiber glass of claim 21.

27. The cementatious body of claim 26 wherein said fiber glass comprises less than about 0.25% by weight iron oxide.

28. The cementatious body of claim 27 wherein said fiber glass comprises less than about 0.1% by weight iron oxide.

STATEMENT UNDER ARTICLE 19

Claims 1-27 have been replaced by new claims 1-28 to clearly define the claimed invention over the prior art. Applicant submits that the invention as currently claimed is novel and unobvious over the references contained in the International Search Report.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/01905

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. [3] C03C 3/04, 13/00; C04B 7/02
U.S. CL. 106/99; 501/27, 35, 70, 73

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	106/99 501/27, 35, 70, 73

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X,Y	US, A, 3,687,850 Published 29 August 1972, Gagin	1-27
X,Y	US, A, 4,046,948 Published 06 September 1977, Zlochower	1-27
X,Y	US, A, 4,066,466 Published 03 January 1978, Neely, Jr.	1-27
X,Y	US, A, 4,199,364 Published 22 April 1980, Neely	1-27
X,Y	SU, A, 455,027 Published 31 March 1975	1-27
X,Y	JP, A, 52-4519 Published 13 January 1977	1-27
X,Y	JP, A, 53-7729 Published 24 January 1978	1-27
X,Y	JP, A, 55-3367 Published 11 January 1980	1-27
X,Y	JP, A, 56-5352 Published 20 January 1981	1-27

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
15 January 1985	28 JAN 1985
International Searching Authority [1]	**Signature of Authorized Officer [10]**
ISA/US	Mark Bell *Mark Bell*

WEST

International Application No. PCT/US84/01905

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X,Y	GB, A, 2,083,017 Published 17 March 1982	1-27
Y	WO, A, WO82/03386 Published 14 October 1982	5-9 and 17
Y	N, BANBA et al.; "Safety Evaluation of Simulated High Level Waste Glass Products (I) (Thermal Stability)", from INIS Atom index 1980 11(24) Abstract No. 571,744 Tokai Res Establ, Japan At. Energy Res. Inst., Tokai, Japan, Report 1980, JAERI-M-8706, 20 pages	5-9 and 17

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers........, because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers........, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.